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Synthesizing aluminum particles towards controlling electrostatic discharge ignition sensitivity

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1. Introduction

Composite energetic materials (CEM) are defined here as mixtures of aluminum (Al) fuel and metal oxide particles, that ignite to produce exothermic chemical energy. With the advent of nano technology, nano Al fuel particles have shown heightened reactivity compared to their micron scale counterparts [1–3]. Safely handling these powder mixtures requires a thorough understanding of their electrostatic ignition sensitivity yet very few studies on electrostatic discharge (ESD) ignition have been reported in the literature [4–6].

Most ESD ignition research is performed for the discharge of electric energy into a sample rather than by pouring induced inter particle transport (e.g., electrostatic sensitivity that can occur from pouring a powder sample). An interesting finding from studying the literature on electrostatic ignition of powders is that a paradox exists regarding the electrical properties of the powder and the corresponding electrostatic ignition behavior. Glor [7] studied dust particles that had accumulated a charge through inter particle transport. He found that as the powder's electrical conductivity decreased, so does the minimum ignition energy. In other words, materials with a decreased conductivity are more readily ignited by ESD [7]. In contrast, Foley et al.'s [8] study on Al–CuO showed that increasing electrical conductivity using additives actually decreased the minimum ignition energy of the mixture. A striking difference in these two studies is the way in which the electrical stimuli were introduced to the sample. For Glor [7] electrostatic charge accumulated within the sample, while in Foley et al. [8] the electrostatic charge was discharged into the sample. This paradox poses new research questions that have potential for impactful development in this field.

As a first step, we examined electrostatic discharge (ESD) ignition sensitivity of nine different CEM formulations, limiting the study to only micron Al inclusion [6]. The results showed that at the highest setting on the ESD apparatus (i.e., which corresponded to 100 mJ), only Al–CuO ignited and its corresponding electrical conductivity was measured to be two orders of magnitude above the next mixture, Al–MoO_3 which did not ignite (i.e., 1246 compared with 40 nS/m, respectively). This was the first study to correlate electrical conductivity to ESD ignition sensitivity in energetic materials [6].

The influence of alumina in ESD ignition sensitivity was further studied in Ref. [9]. Specifically, Weir et al. [9] examined the electrical conductance and ESD ignition sensitivity of aluminum and molybdenum trioxide (Al + MoO_3) with varying Al particle size ranging from nano to micron scales. The results showed that as

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particle diameter decreased (and alumina concentration increased) the electrical conductance increased by 7 orders of magnitude and minimum ignition energy required for ESD ignition reduced accordingly. On the other hand, discretely added alumina particles significantly reduce the mixtures electrical conductivity, desensi tizing the mixture to ESD ignition. This study revealed that the alumina shell may play a significant role in spurring ignition in Al + MoO_3 by accumulating charge and acting as a capacitive network, in contrast to discretely added alumina particles.

The objective of this work is to understand how the electrical conductivity and ESD ignition sensitivity of Al + MoO_3 varies as a function of the thickness of the alumina passivation shell sur rounding the Al particles. To accomplish this objective, nano scale Al particles were synthesized with varying shell thicknesses and combined with nano scale MoO_3 particles. The mixture was further studied for electrical conductivity measurements and ESD ignition sensitivity quantified in terms of ignition delay time.

2. Experimental

The Al particles were supplied by Sigma Aldrich and had an average particle diameter of 95 nm. The MoO_3 particles were pur chased from Nanostructured and Amorphous Materials Inc. and had an average platelet size of 380 nm. The Al particles were oxidized in an isothermal oven to increase the thickness of the Al_2O_3 shell; thereby synthesizing particles with controlled shell thicknesses. It is noted that the overall particle diameter does not change, such that the shell thickness grows at the interface of aluminum and alumina and as alumina concentration increases, aluminum correspondingly decreases.

2.1. Material synthesis and preparation

A thermogravimetric analyzer (TGA), model STA 409 PC by Netzsch, was used to observe the weight gain of Al particles as the Al oxidized to Al_2O_3. During oxidation in the TGA, 11.48 mg of Al powder was held in a platinum crucible while the temperature increased at a rate of 40 °C per minute in a controlled environment of ultra high purity oxygen. The oven continued to heat until 480 °C, a temperature that provided reasonable reaction rates where oxidation and shell growth was observed. The Al sample remained in the isothermal environment for 180 min as the mass gain was monitored. The precision of the change in mass of the sample in the TGA had a variance of 0.001 mg. This data was used to control oxide shell growth on larger quantities of aluminum powder.

A Neytech Qex oven was used to oxidize Al particles in an isothermal oxygen environment. Ultra high purity oxygen was purged in the oven chamber at a flow rate of 180 cm^3/min for 10 min. This procedure ensured that the volume was flushed five times and had a statistical purity of 99% of oxygen in the oven chamber. The Qex oven was set to have a temperature ramp rate of 200 °C/min and a temperature of 480 °C. The settings were pro grammed in the oven for automated control and repeatability be tween oxidation procedures. Six samples of 0.9 g of Al powder were prepared for each oxidation cycle. Once the chamber was purged and the temperature of 480 °C was reached, the Al powder remained in the oven for various durations ranging from 8 to 150 min. This variable oxidation time provided different alumina shell thicknesses.

A transmission electron microscope (TEM), model Jeol JEM 2100, was used to examine the Al particles and measure the thickness of the alumina shell with Gatan image analysis software to measure the thickness of the alumina shell. Thickness mea surements were taken from at least three different locations on several Al particles. Fig. 1 shows three representative images of the Al particles taken from the TEM.

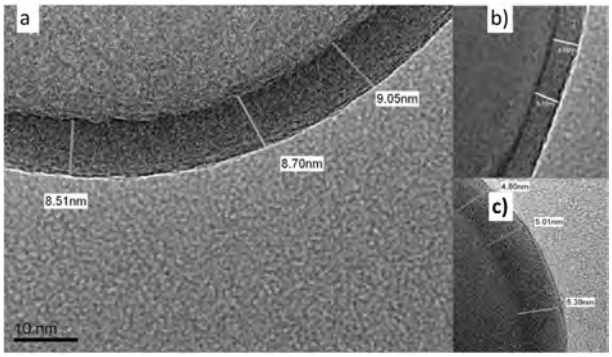

Fig. 1. TEM images of the alumina shell after oxidation times of a) 150 min, b) 8 min, and c) 30 min.

The percent of active Al by weight (Y) was calculated using Eq. (1),

$$\frac{R^3}{(R \quad \delta)^3} \quad \frac{\rho_m}{\rho_{mo}}\left(\frac{1}{(Y)} \quad 1\right) + 1 \tag{1}$$

where R is the average particle radius, δ is the Al_2O_3 shell thickness, and ρ is the density of the metal (m) and metal oxide (mo). The average shell thickness and the percent of active Al content are listed in Table 1 for all treated Al powders.

The Al + MoO_3 mixtures were prepared to an equivalence ratio of 1.0, corresponding to stoichiometric conditions. Details of this mixing procedure are reported in Ref. [10].

2.2. Experimental setup

An acrylic channel was loaded with 58 mg of the powder, which was pressed into a pellet within the channel. The pellet occupied a volume of 31 mm^3 and had a bulk density of 1.89 g/cm^3. The bulk density of the pellet was calculated to be 50% of the theoretical maximum density (TMD). Two copper electrodes were positioned to cover the openings in the channel such that the tips of the electrodes were in contact with the surface of the pellet as shown in Fig. 2. A voltage potential was applied to the electrodes and when greater than the dielectric strength of the pellet material, a spark was generated which ignited the pellet. The voltage source used in these experiments was an electrostatic discharge (ESD) tester that is a human body model developed by Franklin Applied Physics [6]. A human body model transfers charge from a capacitor (human) to another object. The range of voltage output is 1–10 kV which is stored in a 0.002 μF capacitor producing up to 100 mJ of energy.

A current monitor, model 2878 from Pearson Electronics, was used to measure the electric charge released by the ESD tester. A

Table 1
Thickness of Al_2O_3 shell and weight percent active Al content for all oxidized Al particles.

Oxidation time (min)	Al_2O_3 thickness (nm)	Wt % active Al
0	2.7	78.1
8	3.3	73.9
15	4.5	66.3
30	4.6	65.7
60	5.7	59.4
90	6.7	54.2
150	8.3	46.7

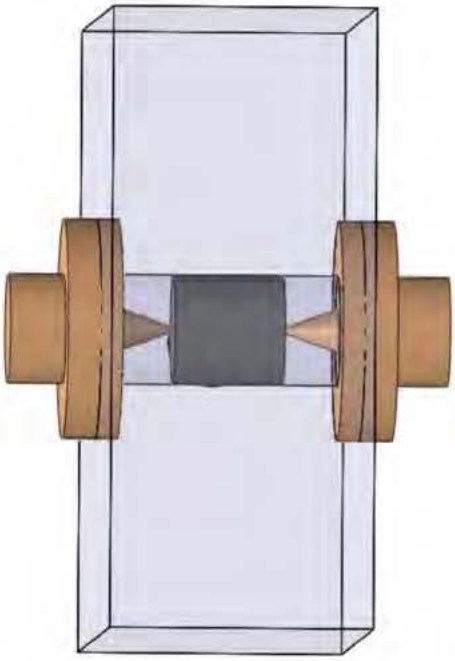

Fig. 2. Electrodes in contact with the pellet in the acrylic channel.

high voltage probe, model P6015A from Tektronix, reduced the voltage 1000 times, enabling the use of oscilloscopes to record the voltage output. Ignition delay time was measured as the length of time between the spark and the instant that luminosity produced a slope of ten, which was the maximum slope observed for all the tests, and detected using a photo detector; model DET210 from Thorlabs (see Fig. 3). The ignition energy was determined from the simultaneous current and voltage measurements.

3. Results

3.1. Ignition delay

As the voltage potential between the two electrodes increased beyond the electric field strength of the medium, a spark bridged the electrode gap and ignited the CEM. Fig. 4 is a good represen tation of the voltage, current, and luminosity for all tests. As the spark bridged the electrode gap, the voltage decreased and the current increased as shown in Fig. 4a. The length of time between the spark and the instant that luminosity produced a slope of ten

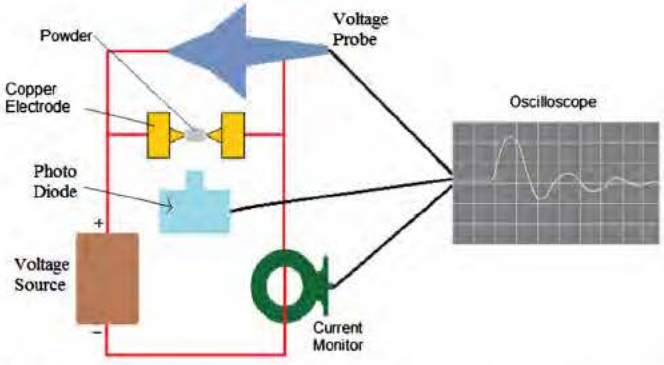

Fig. 3. Electrical circuit used to monitor voltage and current and measure time delay of the reaction.

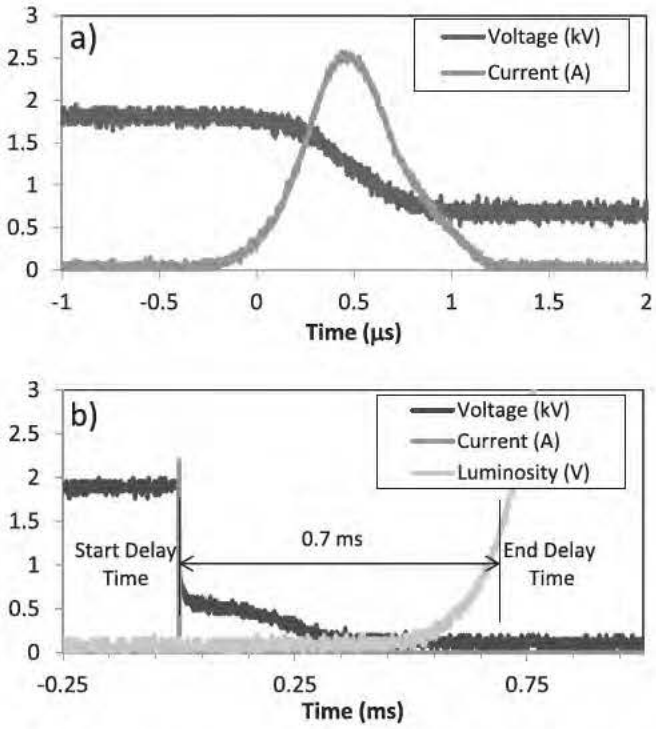

Fig. 4. Voltage, current, and luminosity depicting time delay for Al + MoO_3.

(Fig. 4b) (i.e., corresponding to the maximum slope observed for all the tests) was recorded as the ignition delay for the reaction.

The ignition time delay tests were conducted for CEM mixtures containing each batch of oxidized Al powder identified in Table 1 combined with MoO_3. Three samples were tested for each Al powder with varied shell thickness and the ignition time delay is shown in Fig. 5.

All CEMs were deemed ESD ignition sensitive because all ignited below the maximum energy threshold of 100 mJ supplied by the ESD apparatus. The thinner shelled Al powders experienced the fastest ignition. Ignition delay increased as the Al_2O_3 shell thickness increased. The voltage required to ignite the powders also increased as the Al_2O_3 shell thickness increased (Fig. 6).

3.2. Joule heating of an aluminum particle

The joule heating of a single Al particle was modeled using COMSOL Multiphysics. The equation used for calculating joule heating is the time dependent energy equation for incompressible flow as shown in Eq. (2).

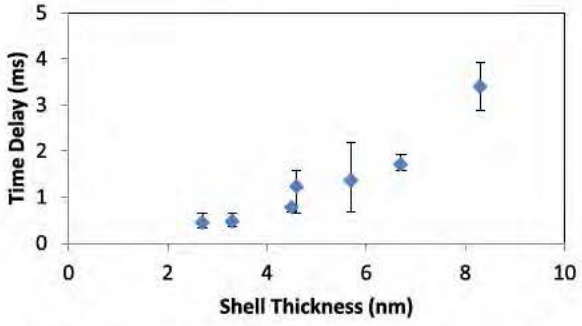

Fig. 5. Ignition time delay for Al + MoO_3 reactions with varying alumina shell thicknesses.

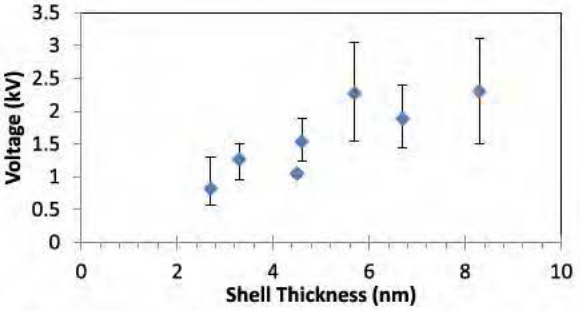

Fig. 6. Ignition voltage for Al + MoO_3 reactions with varying alumina shell thicknesses.

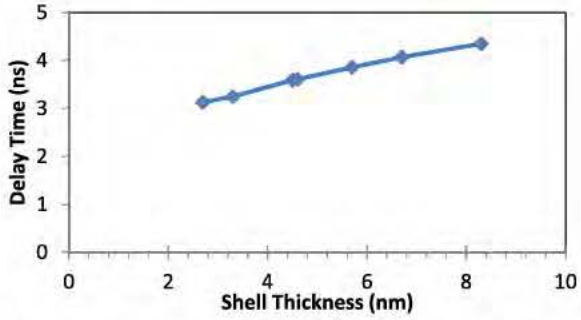

Fig. 8. Predicted ignition delay for a single Al particle with varying alumina shell thicknesses.

$$\rho C_P \frac{\partial T}{\partial t} + \rho C_P \mathbf{u}\cdot\nabla T \qquad \nabla\cdot(k\nabla T) + J\cdot E \tag{2}$$

In Eq. (2), ρ is the density, C_p is the specific heat, T is temperature, t is time, u is a velocity vector, J is the current density, and E is the electric field strength. A single Al particle was modeled and assumed to have a contact point with another particle on its top, bottom, front, back, left, and right surfaces. A current of 1 Amp entered the Al particle at one contact point while the rest of the contact points were held at ground potential. In the model, the initial temperature of the Al particle was 20 °C and an initial electric potential was 0 V. Because convective cooling was neglected in the model due to the fast ignition of the particle, the boundary was insulated thermally. The spherical Al particle was assumed to have a solid Al core with an axisymmetric temperature distribution. The model also assumes homogeneous metals within the particle when in reality, the metals are not homogeneous and contain impurities and cracks.

The model results for transient heating of an Al particle with an Al_2O_3 shell thickness of 2.7 nm are shown in Fig. 7. As current travels through a single particle, temperature quickly increased with time. Since the melting temperatures of the fuel and oxide are similar, 933 and 1068 K respectively, ignition of the particle was assumed to occur at the melting temperature of Al [11] and the model predicts ignition times for these conditions to range from 3.0 to 5.0 ns (Fig. 7). Note that the modeled ignition time is significantly less than the experimentally measured ignition time (Fig. 5). The main reason for this difference is that the model predicts ignition delay for a single particle whereas in the experiments, the delay is measured for a macroscopic collection of particles. The heat transfer among neighboring particles within the random media of the reactant sample is not accounted for in this model and beyond the scope of this study. But it is noted, that for considering thermal diffusion only through a single aluminum particle, the characteristic evaporation time assuming a continuum droplet evaporation model was calculated to be on the order of $4.6 \times 10^6\, d^2$ where d is the aluminum particle diameter [12]. In this model applied to the particles studied here, the characteristic thermal evaporation time is approximately 50 ns, and greater than the joule heating times determined here. Instead, the trend in behavior as shell thickness is varied is of interest and can be correlated to ignition delay times.

Fig. 8 shows the ignition delay of the Al particles for all the Al_2O_3 shell thicknesses predicted by the COMSOL model.

The model shows that the ignition delay increases as the shell thickness increases. This result is consistent with the measured delay (Fig. 5) and implies that the increase in shell thickness retards thermal energy buildup within a single particle such that ignition delay times are extended. This result implies that joule heating is an Al ignition mechanism for electric stimuli.

The electrical conductivity was also measured using a high resistance low conductance meter and a two point probe method [6]. Fig. 9 shows that electrical conductivity decreases as shell thickness increases.

As the percent of Al_2O_3 increases, the electrical conductivity decreases. Also, as the percent of Al_2O_3 content increases, the electrical resistance increases and the current decreases, with a constant voltage. With more resistance impeding the flow of electric energy, joule heating of the aluminum core may be delayed thereby requiring more time to reach Al melting temperature and ignition.

4. Discussion

These results show that all Al + MoO_3 samples were ESD ignition sensitive (Fig. 5) but their sensitivity is controlled by the shell thickness surrounding the Al particle. Increasing shell thickness from 2.7 to 8.3 nm increases the ignition delay time up to 4 ms and requires up to 1000 V more electric input to achieve ignition (Figs. 5 and 6). Modeling the heat transfer through a single Al particle subjected to similar electric input conditions reveals a comparable

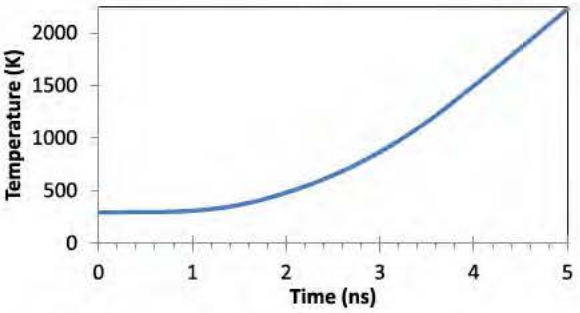

Fig. 7. Temperature of Al particle from joule heating COMSOL model.

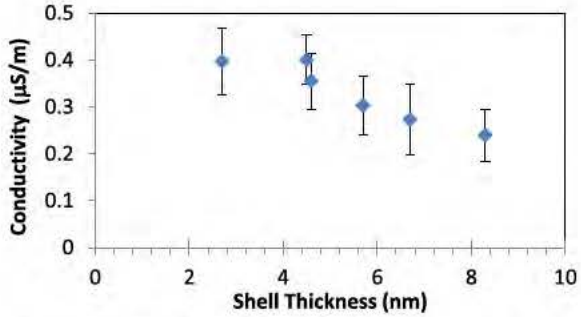

Fig. 9. Electrical conductivity of Al + MoO_3 powders with a varying Al_2O_3 shell thickness.

trend observed experimentally: increasing shell thickness leads to increasing ignition delay time and decreasing electrical conduc tivity (Figs. 8 and 9). Alumina retards energy propagation in the core–shell structure of the aluminum–alumina particle and this is represented by the COMSOL model (Figs. 7 and 8). This finding also suggests that joule heating is the primary mechanism of ignition for ESD stimuli.

5. Conclusion

Aluminum particles were synthesized with varying oxide shell thicknesses that ranged between 2.7 nm and 8.3 nm. Electrostatic discharge was used to ignite Al + MoO_3 and the ignition delay time was measured. The physics were also modeled using COMSOL Multiphysics software to approximate the temperature increase of an Al particle due to joule heating. The measured and modeled results both show similar trends in that the ignition delay increased as the Al_2O_3 shell thickness increased. The increase in ignition delay time suggests that the ESD ignition mechanism is joule heating because the model calculates transient temperatures based on transforming electrical stimuli into thermal energy. Alumina re tards energy buildup within the particle such that thicker alumina shells result in longer ignition delay times. The results reveal that the current flow through the particle is a controlling parameter for ignition and a thicker shell increases resistance and therefore lowers the amount of current flowing through the aluminum core.

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